

# Regulating the distribution of iron active sites on $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> via Mn-modified $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> for NH<sub>3</sub>-SCR

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## ABSTRACT

Developing below 150 °C highly activity and broad reaction window catalysts has been challenging by using Fe-based catalysts for NH<sub>3</sub>-SCR. The octahedral Fe<sup>3+</sup> (Fe<sub>Oh</sub><sup>3+</sup>) sites exist in hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) and maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) are inactive for NH<sub>3</sub>-SCR due to the redox circle of Fe<sup>2+</sup>→Fe<sup>3+</sup> reliance on the distribution of iron sites in crystal structure. Here we modified the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> crystal structure by substituting part inactive Fe<sub>Oh</sub><sup>3+</sup> sites with catalytically active Mn<sub>Oh</sub><sup>3+</sup> sites, which promoted the formation of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> to generate the active tetrahedral Fe<sup>3+</sup> (Fe<sub>Td</sub><sup>3+</sup>) sites and enhanced the magnetism of the Fe<sub>1-y</sub>Mn<sub>y</sub>O<sub>x</sub>. The strong Fe-O-Mn interaction established by crystal coordinative configurations not only boosted the formation of NO<sub>2</sub> but also facilitated the Brønsted acid circle. Surprisingly, the Fe<sub>0.85</sub>Mn<sub>0.15</sub>O<sub>x</sub> exhibited the superior low temperature NH<sub>3</sub>-SCR activity, with NO<sub>x</sub> conversion above 100% at 100–275 °C under a GHSV of 60000 h<sup>-1</sup>.

## 1. Introduction

Nitrogen oxides that containing NO and NO<sub>2</sub> mainly emitted by power stations, factories and automobiles have made great contributions to air pollution, significantly affecting global tropospheric chemistry and seriously endangering human health [1,2]. At present, it is considered to be an efficient and practical method to use vanadium metal oxide as catalyst to achieve efficient NO elimination in NH<sub>3</sub>-SCR technology. Developing environmental-friendly and low-temperature (LT) high-efficiency catalysts is necessary due to the poor catalytic activity below 150 °C and secondary pollution caused by serious biotoxicity hinder the scope of applications of vanadium-based catalysts [3].

Iron-based catalysts have attracted much attention from researchers because of environment-friendly, low economic cost and catalytic stability in the middle and high temperature window for NH<sub>3</sub>-SCR. Among the crystalline phases of Fe<sub>2</sub>O<sub>3</sub>, maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) and hematite

( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) are the most widely investigated for NH<sub>3</sub>-SCR [4,5]. Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) has a rhombohedral centered hexagonal structure consisting only of Fe<sub>Oh</sub><sup>3+</sup> sites in which Fe<sup>3+</sup> ions occupying the octahedral oxygen center, maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) has a spinel structure centered on tetrahedral Fe<sup>3+</sup> (Fe<sub>Td</sub><sup>3+</sup>) and octahedral Fe<sup>3+</sup> (Fe<sub>Oh</sub><sup>3+</sup>) sites [6]. Qu et al. creatively demonstrated that Fe<sub>Td</sub><sup>3+</sup> sites as the catalytically active sites (CASS) in NH<sub>3</sub>-SCR by substituting the Fe<sub>Td</sub><sup>3+</sup> sites and Fe<sub>Oh</sub><sup>3+</sup> sites with inactive Ti<sup>4+</sup> or Zn<sup>2+</sup> respectively and found the electron transfer between Fe<sup>3+</sup> and Fe<sup>2+</sup> is promoted in Fe<sub>Td</sub><sup>3+</sup> sites compared with Fe<sub>Oh</sub><sup>3+</sup> sites [7]. Liu et al. found the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> catalysts exhibited lower catalytic performance than  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> below 200 °C due to stable nitrates more easily formed on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> surface than  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and blocked the active sites [8]. Wen et al. prepared FeNb<sub>0.4</sub>O<sub>x</sub>-C catalyst by coprecipitation with the assistance of CTAB to induce generate  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. The interaction between Fe-Nb and brought about more active sites hence enhanced the NO<sub>x</sub> conversion [9]. Despite many achievements have been made in the study of iron oxides in NH<sub>3</sub>-SCR, developing the wide operating temperature window and

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the excellent LT activity (below  $\sim 150^\circ\text{C}$ ) remains a crucial bottleneck for  $\text{Fe}_2\text{O}_3$ -based catalysts. The performance of representative of iron-based catalysts for  $\text{NH}_3$ -SCR in recent five years is summarized in Table 1.

Manganese oxides with variable valence states and excellent redox ability are commonly investigated for  $\text{NH}_3$ -SCR. Although manganese-based materials showing an excellent LT SCR activity, restraining their practical applications because of sensitivity to  $\text{SO}_2$ , poor  $\text{N}_2$  selectivity and show narrow working temperature window [10,11]. However, manganese oxides as additives for other metal oxides can enhance the redox ability and increase Brønsted acid sites on  $\text{NH}_3$ -SCR catalysts [12]. The flexible valence states of manganese oxides facilitate the electronic transfer with other metal ions and formation of abundant active oxygen, thus promoting the NO oxidize to  $\text{NO}_2$  and trigger the “Fast SCR” reaction at low temperatures [13,14]. Zhang et al. found that Mn doping can optimize the structure of  $\gamma\text{-Fe}_2\text{O}_3$  and form Fe-Mn solid solution, thus improving the SCR activity at low temperature [49]. Lai et al. report on a Fe-Mn system, the existence of manganese causes the lattice contraction of  $\gamma\text{-Fe}_2\text{O}_3$  and increases the activation energy of construct  $\alpha\text{-Fe}_2\text{O}_3$ , thus maintaining the crystal phase of  $\gamma\text{-Fe}_2\text{O}_3$  at high temperature [15].

Transformation of crystal phase structure and CAs are essential in  $\text{NH}_3$ -SCR for iron-based oxides due to the formation of  $\alpha\text{-Fe}_2\text{O}_3$  above  $320^\circ\text{C}$ . Relationship between crystal structure and CAs of  $\text{Fe}_2\text{O}_3$  is crucial for elaborate any catalytic reaction mechanism and for the logical devise of high- efficient and low-temperature  $\text{NH}_3$ -SCR catalysts. However, the distribution of the doping element and transformation of crystal phase leads to the change of CAs in crystal structure of  $\text{Fe}_2\text{O}_3$  are seldom investigated on  $\text{NH}_3$ -SCR. In this work, to induce the transition from  $\alpha\text{-Fe}_2\text{O}_3$  to  $\gamma\text{-Fe}_2\text{O}_3$  structure and generate more active  $\text{Fe}^{3+}$  CAs of the iron oxide catalyst, we have modified the  $\text{Fe}_2\text{O}_3$  crystal structure by substituting part inactive  $\text{Fe}^{3+}_{\text{th}}$  sites with catalytically active  $\text{Mn}^{3+}_{\text{th}}$  sites. Herein, a series of  $\text{Fe}_{1-y}\text{Mn}_y\text{O}_x$  was prepared by sol-gel strategy, compared with pure  $\text{Fe}_2\text{O}_3$ , the  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  catalyst exhibited the superior LT catalytic performance and extensive reaction window.

## 2. Experimental section

### 2.1. Catalyst preparation

The  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\gamma\text{-Fe}_2\text{O}_3$ ,  $\gamma\text{-Mn}_2\text{O}_3$  and  $\text{Fe}_{1-y}\text{Mn}_y\text{O}_x$  series catalysts were acquired by sol-gel strategy. First, a 10 ml mixed solution containing 4.04 g of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and a specified amount of Mn ( $\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (The molar ratio of Mn/Fe atoms is contained within range 0–20%) was prepared with deionized water. Second, the mixed solution is then added drop by drop to the 10 ml deionized aqueous solution of citric acid monohydrate (0.73 g/ml). Third, the precursor solution was continuously mixed for 0.5 h, then 30 mg polyethylene glycol (PEG 2000) was added and transferred to a magnetic stirring oil bath at  $80^\circ\text{C}$  for 4 h to obtain a stable gel. Next, the gel was dried at  $100^\circ\text{C}$  for 12 h. Lastly, the catalyst was obtained by grinding the dried material into powder and calcining it at  $350^\circ\text{C}$  in air for 4 h.  $\gamma\text{-Fe}_2\text{O}_3$  acquired by calcined at  $250^\circ\text{C}$  for 2 h. The catalyst is named after the proportion of doped manganese in the total amount of metal atoms. For instance, the  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  catalyst contains 15% of Mn in the total amount of metal atoms.

### 2.2. Catalysts characterization

X-ray diffraction (XRD) data of the catalysts were collected on a Bruker D8 with Cu  $\text{K}\alpha$  radiation at 40 kV and 30 mA and the scanning range was set at  $2\theta$  of  $10\text{--}80^\circ$  with a scanning speed of  $10^\circ/\text{min}$ .

The morphology and microstructure of the samples were observed by field emission scanning electron microscopy (SEM) at 20 kV (FEI Quattro S, Czech).

The energy-dispersive X-ray spectroscopy (EDS) images were

**Table 1**

Representative of iron-based catalysts for the  $\text{NH}_3$ -SCR in recent five years.

catalysts	preparation method	reaction condition	NO conversion	ref
Fe-Ce	sol-gel	NO = $\text{NH}_3$ = 500 ppm, 5 vol% $\text{O}_2$ , GHSV = $90000\text{ h}^{-1}$	$\sim 100\%$ , (200–300 $^\circ\text{C}$ )	[4]
Fe-Nb	co-precipitation	NO = $\text{NH}_3$ = 500 ppm, 5 vol% $\text{O}_2$ , GHSV = $250000\text{ h}^{-1}$	$> 90\%$ , (250–400 $^\circ\text{C}$ )	[9]
Fe-Ce-S	co-precipitation	NO = $\text{NH}_3$ = 500 ppm, 5 vol% $\text{O}_2$ , GHSV = $100000\text{ h}^{-1}$	$\sim 100\%$ , (225–350 $^\circ\text{C}$ )	[16]
Fe-V-Ti	co-precipitation	NO = $\text{NH}_3$ = 500 ppm, 5 vol% $\text{O}_2$ , GHSV = $200000\text{ h}^{-1}$	$\sim 100\%$ , (225–375 $^\circ\text{C}$ )	[17]
$\text{FeMnTiO}_x$ -tourmaline	sol-gel	NO = $\text{NH}_3$ = 800 ppm, 5 vol% $\text{O}_2$ , GHSV = $50000\text{ h}^{-1}$	$> 80\%$ , (160–380 $^\circ\text{C}$ )	[18]
$\text{SO}_4^{2-}/\alpha\text{-Fe}_2\text{O}_3$	impregnation	NO = $\text{NH}_3$ = 600 ppm, 5 vol% $\text{O}_2$ , GHSV = $60000\text{ h}^{-1}$	$\sim 100\%$ , (275–400 $^\circ\text{C}$ )	[19]
$\text{FeVO}_4/\text{CeO}_2$	sol-gel	NO = $\text{NH}_3$ = 500 ppm, 5 vol% $\text{O}_2$ , GHSV = $80000\text{ h}^{-1}$	$> 90\%$ , (225–350 $^\circ\text{C}$ )	[20]
Fe-Mn-Mo/ $\text{TiO}_2$	impregnation	NO = $\text{NH}_3$ = 400 ppm, 3 vol% $\text{O}_2$ , GHSV = $30000\text{ h}^{-1}$	$\sim 100\%$ , (250–300 $^\circ\text{C}$ )	[21]
Fe-Cu	urea-assisted	NO = $\text{NH}_3$ = 500 ppm, 3 vol% $\text{O}_2$ , GHSV = $60000\text{ h}^{-1}$	$> 90\%$ , (150–275 $^\circ\text{C}$ )	[50]
$\text{Fe}_2\text{O}_3 \cdot \text{SO}_4^{2-}/(\text{TiO}_2\text{--ZrO}_2)$	impregnation	NO = $\text{NH}_3$ = 500 ppm, 3 vol% $\text{O}_2$ , GHSV = $47000\text{ h}^{-1}$	$\sim 100\%$ , (300–500 $^\circ\text{C}$ )	[51]
Ti- $\text{Fe}_2\text{O}_3$	co-precipitation	NO = $\text{NH}_3$ = 600 ppm, 3 vol% $\text{O}_2$ , GHSV = $72000\text{ h}^{-1}$	$> 90\%$ , (210–350 $^\circ\text{C}$ )	[52]
$\text{CeO}_2\text{--Fe}_2\text{O}_3\text{--MoO}_3$	impregnation	NO = $\text{NH}_3$ = 500 ppm, 5 vol% $\text{O}_2$ , GHSV = $75000\text{ h}^{-1}$	$> 90\%$ , (225–350 $^\circ\text{C}$ )	[53]
$\text{TiO}_2@(\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3)$	impregnation	NO = $\text{NH}_3$ = 500 ppm, 5 vol% $\text{O}_2$ , GHSV = $20000\text{ h}^{-1}$	$> 90\%$ , (220–420 $^\circ\text{C}$ )	[54]
MnFe-TOS	hydrothermal	NO = $\text{NH}_3$ = 500 ppm, 5 vol% $\text{O}_2$ , GHSV = $30000\text{ h}^{-1}$	$> 80\%$ , (180–380 $^\circ\text{C}$ )	[55]
Zr/Fe-SSZ-13	hydrotherma	NO = 1000 ppm, $\text{NH}_3$ = 1100 ppm, 5 vol% $\text{O}_2$ , GHSV = $30000\text{ h}^{-1}$	$> 90\%$ , (350–575 $^\circ\text{C}$ )	[56]
Fe-CePO4	co-precipitation	NO = $\text{NH}_3$ = 500 ppm, 5 vol% $\text{O}_2$ , GHSV = $60000\text{ h}^{-1}$	$\sim 100\%$ , (240–380 $^\circ\text{C}$ )	[57]
Fe-Nb-Ti	sol-gel	NO = $\text{NH}_3$ = 500 ppm, 4 vol% $\text{O}_2$ , GHSV = $24000\text{ h}^{-1}$	$> 80\%$ , ( $\sim 200^\circ\text{C}$ )	[58]
Fe-OMS-2	hydrothermal	NO = $\text{NH}_3$ = 500 ppm, 5 vol% $\text{O}_2$ , 8 vol% $\text{H}_2\text{O}$ , GHSV = $40000\text{ h}^{-1}$	$> 90\%$ , (125–300 $^\circ\text{C}$ )	[59]

(continued on next page)

Table 1 (continued)

catalysts	preparation method	reaction condition	NO conversion	ref
WO <sub>3</sub> -FeO <sub>x</sub>	solvent-free	NO = NH <sub>3</sub> = 600 ppm, 5 vol% O <sub>2</sub> , GHSV = 60000 h <sup>-1</sup>	~100%, (250–450 °C)	[60]

obtained by the Tecnai G2 F20 S-TWIN instrument of FEI Company, the highresolution transmission electron microscope (HRTEM) images were acquired under an accelerating voltage of 200 kV. Test preparation: ultrasonic the sample in ethanol solution for 10 min, then drop the sample solution into the copper mesh for testing.

The N<sub>2</sub> adsorption-desorption curve was tested on Micrometric Stritar3020 at a temperature of 77 K and the samples were pretreated at 300 °C for 4 h. The pore size distribution and specific surface area of the catalyst were calculated using the Barrett-Joyner-Halenda (BJH) method and the Brunauer-Emmet-Teller (BET) equation.

In situ DRIFTS data were collected in Nicolet IS50 FT-IR spectrometer with a resolution of 4 cm<sup>-1</sup> and a scan count of 32. A certain amount of the catalyst was filled in the reaction cell and pretreated for 0.5 h N<sub>2</sub> purging at 110 °C (pretreatment temperature at 300 °C for NH<sub>3</sub> adsorption-desorption) and the background image is obtained at 50–300 °C (50 °C each step) during the sample cooling process. The sample spectrum was collected within 50–300 °C after the pre-adsorption of the reaction gas for 1 h. Test conditions: NO = NH<sub>3</sub> = 500 ppm, O<sub>2</sub> = 5 vol%, balance N<sub>2</sub> and GHSV = 60,000 h<sup>-1</sup>.

H<sub>2</sub>-TPR and O<sub>2</sub>/NH<sub>3</sub>-TPD experiments were performed using a FINESORB-3010 automatic chemical adsorption instrument. All samples used for testing are 40–60 mesh in size and the gas flow rate used is 10 ml/min. For H<sub>2</sub>-TPR, 25 mg samples were pretreated at 110 °C in N<sub>2</sub> atmosphere for 1 h. The H<sub>2</sub>-Ar mixture (7 vol% H<sub>2</sub>, Ar as the equilibrium gas) was introduced as reducing gas pre-adsorption for 30 min after samples cooled to room temperature. For O<sub>2</sub>-TPD or NH<sub>3</sub>-TPD, 50 mg samples were pretreated at 200 °C or 300 °C for 1 h in He stream. The O<sub>2</sub> (pure O<sub>2</sub>) or NH<sub>3</sub> (5 vol% NH<sub>3</sub>, N<sub>2</sub> as the equilibrium gas) was introduced as adsorption gas pre-adsorption for 1 h after samples cooled to room temperature and then purging in the He atmosphere for 30 min. Finally, the samples were raised from room temperature to 800 °C at a heating rate of 10 °C/min, and the data of H<sub>2</sub>-TPR, O<sub>2</sub>-TPD and NH<sub>3</sub>-TPD was collected by thermal conductivity detector (TCD).

X-ray photoelectron spectroscopy (XPS) were carried out on Thermo Fisher Scientific ESCALAB 250XI and the data were corrected based on C 1 s = 284.8 eV.

The hysteresis loop of the catalyst was obtained by vibrating sample magnetometer (VSM) Lake Shore 7404 and the moment measuring range: 5 × 10<sup>-7</sup>–10<sup>-3</sup> emu.

### 2.3. Catalytic performance evaluation

The NO, NO<sub>2</sub> and N<sub>2</sub>O concentration in catalytic reaction was determined by FGA10 flue gas analyzer. A Nicolet IS50 FT-IR spectrometer was used to detect the concentrations of NH<sub>3</sub>. All tests used 40–60 mesh 100 mg samples with a 10 mm O.D. quartz tube. Water vapor in flue gas is produced by FD-WG water vapor generator (Furende Inc). The concentration and composition of reaction gas standard cylinders used are as follows: NO (1250 ppm NO, N<sub>2</sub> as the equilibrium gas), NH<sub>3</sub> (1271 ppm NH<sub>3</sub>, N<sub>2</sub> as the equilibrium gas), O<sub>2</sub> (15% O<sub>2</sub>, N<sub>2</sub> as the equilibrium gas), SO<sub>2</sub> (1027 ppm SO<sub>2</sub>, N<sub>2</sub> as the equilibrium gas). In the reaction process, the flow rate is controlled by using type MT-50–2 J flowmeters to generate defined concentrations.

Reaction conditions: NO = NH<sub>3</sub> = 500 ppm, O<sub>2</sub> = 5 vol%, SO<sub>2</sub> = 25 ppm (when used), H<sub>2</sub>O = 5 vol% (when used). The NO conversion and N<sub>2</sub> selectivity 50–300 °C was calculated as followed

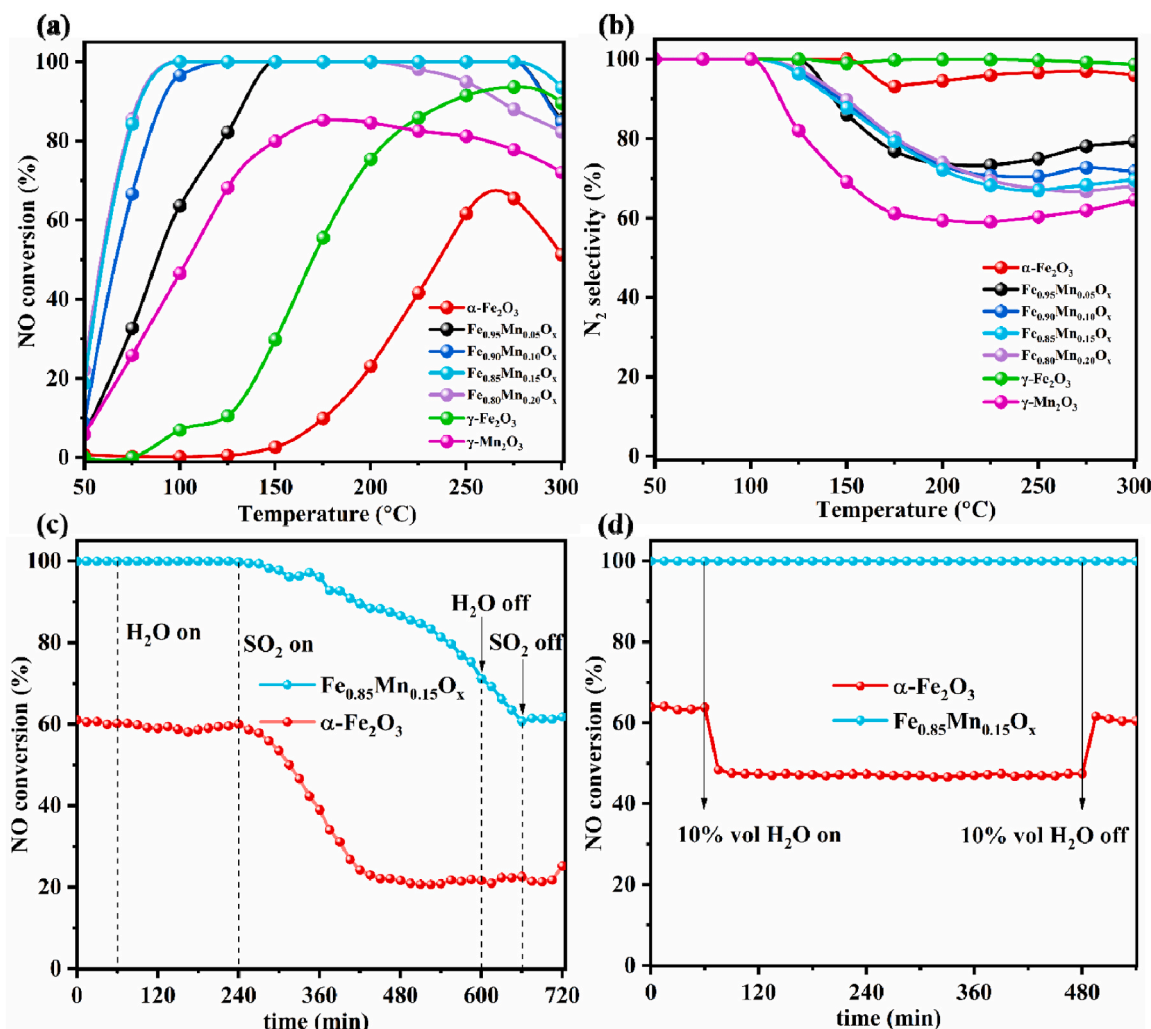
$$\text{NO conversion} = \left[ \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \right] \times 100\%$$

$$\text{N}_2 \text{ selectivity} = \left[ 1 - \frac{2[\text{N}_2\text{O}]_{\text{out}} + [\text{NO}_2]_{\text{out}}}{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}} + [\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}}} \right] \times 100\%$$

## 3. Results and discussion

### 3.1. NH<sub>3</sub>-SCR performance and H<sub>2</sub>O/SO<sub>2</sub> tolerance

In order to study that influence of manganese doping into Fe<sub>2</sub>O<sub>3</sub> on catalytic performance. The low-temperature SCR performance over catalysts were test in the range of 50–300 °C, 25 °C for each step. The results of NO conversion are shown in Fig. 1(a), it can be seen that the highest NO conversion of α-Fe<sub>2</sub>O<sub>3</sub> catalyst only achieve 65% in the 275 °C and inactivity at 50–150 °C. In comparison, the pure γ-Fe<sub>2</sub>O<sub>3</sub> shows ~90% NO conversion at 250–300 °C and γ-Mn<sub>2</sub>O<sub>3</sub> shows ~80% NO conversion at 150–250 °C. However, after the modified the Fe<sub>2</sub>O<sub>3</sub> crystal structure by doping manganese, the NO conversion of the catalysts is improved significantly. It is worth noting that among Fe<sub>2</sub>O<sub>3</sub> and all Fe<sub>1-y</sub>Mn<sub>y</sub>O<sub>x</sub> catalysts, Fe<sub>0.85</sub>Mn<sub>0.15</sub>O<sub>x</sub> exhibits the best NH<sub>3</sub>-SCR performance which achieves above 85% in the 75 °C and nearly 100% within 100–275 °C at a GHSV of 60,000 h<sup>-1</sup>. Moreover, the activity of Fe<sub>1-y</sub>Mn<sub>y</sub>O<sub>x</sub> catalysts is enhance with the manganese content increase from 5% to 20% at low temperatures (50–150 °C) while decrease the activity when the manganese content over 15% at high temperatures (over 200 °C). This means that the introduction of manganese produces more catalytically active sites (CASS) in Fe<sub>1-y</sub>Mn<sub>y</sub>O<sub>x</sub> catalysts for NH<sub>3</sub>-SCR. It was noted that the activity of the Fe<sub>0.80</sub>Mn<sub>0.20</sub>O<sub>x</sub> began to decline at 200 °C, which was mainly caused by the adsorption of NH<sub>3</sub> on acidic sites is weakened and the occurrence of side reaction of NH<sub>3</sub> over-oxidation at high temperatures results in less reductant [22,23]. Thus, the balance in redox circle and acid circle is crucial for Fe<sub>0.85</sub>Mn<sub>0.15</sub>O<sub>x</sub> have the capability to exhibit the superior LT NH<sub>3</sub>-SCR activity and a broad reaction window. The N<sub>2</sub> selectivity of the catalysts for the NH<sub>3</sub>-SCR reaction were calculated and shown in Fig. 1(b). It can be seen that γ-Fe<sub>2</sub>O<sub>3</sub> shows better N<sub>2</sub> selectivity than α-Fe<sub>2</sub>O<sub>3</sub> and γ-Mn<sub>2</sub>O<sub>3</sub> in the whole temperature window and nearly 100%. Notably, compared with pure Fe<sub>2</sub>O<sub>3</sub>, the introduction of Mn caused the production of N<sub>2</sub>O as a by-product at 125 °C (Fig S1), which led to the decrease of the N<sub>2</sub> selectivity of the Fe<sub>1-y</sub>Mn<sub>y</sub>O<sub>x</sub>. In addition, the stability of the Fe<sub>0.85</sub>Mn<sub>0.15</sub>O<sub>x</sub> catalyst was tested and shown in Fig. S2. The Fe<sub>0.85</sub>Mn<sub>0.15</sub>O<sub>x</sub> catalyst can maintain nearly 100% NO conversion and 90% N<sub>2</sub> selectivity at 150 °C for 24 h. The H<sub>2</sub>O and SO<sub>2</sub> resistance over α-Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>0.85</sub>Mn<sub>0.15</sub>O<sub>x</sub> were investigated due to H<sub>2</sub>O and SO<sub>2</sub> are inevitably exist in actual flue gas. As depicted in the Fig. 1(c) and (d). When 5 vol% H<sub>2</sub>O was turned on the reaction gas at 250 °C, α-Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>0.85</sub>Mn<sub>0.15</sub>O<sub>x</sub> catalysts is no obvious fluctuation in 3 h of the NO conversion, however, when we increase the water vapor content from 5 to 10 vol%, it can be seen in the Fig. 1(d), NO conversion of α-Fe<sub>2</sub>O<sub>3</sub> decreases from 63% to 47%, while the NO conversion of Fe<sub>0.85</sub>Mn<sub>0.15</sub>O<sub>x</sub> can still maintain nearly 100%, showing that the excellent water-resistant ability of Fe<sub>0.85</sub>Mn<sub>0.15</sub>O<sub>x</sub> after Mn modified the Fe<sub>2</sub>O<sub>3</sub> crystal structure. In addition, the NO conversion of α-Fe<sub>2</sub>O<sub>3</sub> decreased from 60% to 23% in 3 h when 25 ppm SO<sub>2</sub> was turned on the reaction gas at 250 °C while Fe<sub>0.85</sub>Mn<sub>0.15</sub>O<sub>x</sub> was maintained at ~90% was observed after being tested. This means that the sulfur resistance has been improved by modified the Fe<sub>2</sub>O<sub>3</sub> crystal. Besides, the NO conversion of Fe<sub>0.85</sub>Mn<sub>0.15</sub>O<sub>x</sub> still decrease after turn off 5 vol% H<sub>2</sub>O and irreversible after being poisoned by SO<sub>2</sub>, which means SO<sub>2</sub> is the main reason cause Fe<sub>0.85</sub>Mn<sub>0.15</sub>O<sub>x</sub> inactivation.



**Fig. 1.** NH<sub>3</sub>-SCR performance of catalysts: (a) NO conversion of catalysts; (b) N<sub>2</sub> selectivity of the catalysts for the NH<sub>3</sub>-SCR reaction; (c) The 5 vol% H<sub>2</sub>O and SO<sub>2</sub> tolerance of Fe<sub>0.85</sub>Mn<sub>0.15</sub>O<sub>x</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> at 250 °C; (d) The 10 vol% H<sub>2</sub>O tolerance of Fe<sub>0.85</sub>Mn<sub>0.15</sub>O<sub>x</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> at 250 °C. Reaction conditions: NO = NH<sub>3</sub> = 500 ppm, O<sub>2</sub> = 5 vol%, H<sub>2</sub>O = 5 or 10 vol% (when used), SO<sub>2</sub> = 25 ppm (when used), balance N<sub>2</sub> and GHSV = 60,000 h<sup>-1</sup>.

### 3.2. Structure and morphology

#### 3.2.1. XRD analysis

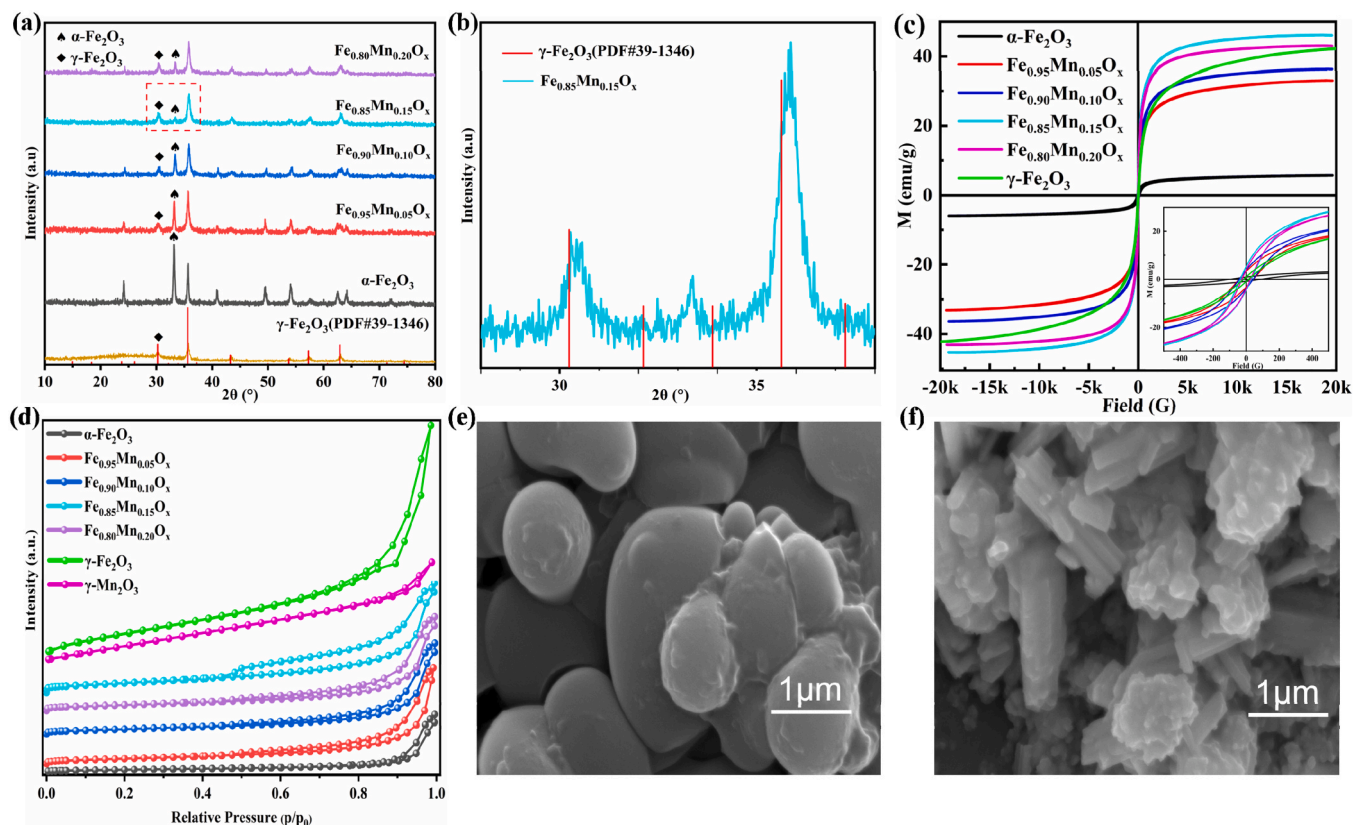
To obtain structural information on the Mn modified the Fe<sub>2</sub>O<sub>3</sub> catalysts. Fig. 2(a) show the XRD spectrum of the Fe<sub>1-y</sub>Mn<sub>y</sub>O<sub>x</sub> catalysts with various manganese-doped contents and pure Fe<sub>2</sub>O<sub>3</sub>. Pure Fe<sub>2</sub>O<sub>3</sub> is identified as hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) with a hexagonal structure (JPCDS Card No. 33-0664) [8,24]. Additionally, there are some new diffraction peaks appeared after doping manganese, while no diffraction peak belongs to MnO<sub>x</sub> can be detected. This distinct shows that Mn doped into the Fe<sub>2</sub>O<sub>3</sub> crystal lattice [25]. The diffraction peaks at 30.3°, 35.7°, 37.4°, 43.5°, 53.9°, 57.5° and 63.1° can be well indexed to  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (JCPDS Card No. 39-1346), corresponding to the lattice planes of (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) [7,8,15]. With increasing manganese content is increased from 5% to 20%, all the intensity of diffraction peaks of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> becoming weaken and the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> gradually increases. This means that the crystalline phase can be induced from  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> to  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> by introducing manganese. Note that all the peaks of Fe<sub>1-y</sub>Mn<sub>y</sub>O<sub>x</sub> clearly shift to larger Bragg angles in comparison to  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. This occurs after substitution of part Fe<sub>Oh</sub><sup>3+</sup> with Mn<sup>3+</sup> in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and generate Fe<sub>Td</sub><sup>3+</sup> of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, which brought about lattice contraction [15]. Furthermore, we calculate the crystallite sizes, lattice constants of (2 2 0) peaks and to quantify the ratio of  $\alpha/\gamma$  Fe<sub>2</sub>O<sub>3</sub> of the Fe<sub>1-y</sub>Mn<sub>y</sub>O<sub>x</sub> catalysts and the results comparison with pure  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> are summarized

in Table 2. In consideration of ionic radius of Fe<sub>Td</sub><sup>3+</sup> (0.49 Å) and Fe<sub>Oh</sub><sup>3+</sup> (0.65 Å), the Mn<sup>3+</sup> (0.58 Å) is smaller than that of Fe<sub>Oh</sub><sup>3+</sup> (0.65 Å) [7], the related changes in the lattice parameters calculated from the (2 0 0) peaks indicating that substitution of part Fe<sub>Oh</sub><sup>3+</sup> with Mn<sup>3+</sup> in Fe<sub>1-y</sub>Mn<sub>y</sub>O<sub>x</sub> after Mn modified. This conclusion is consistent with XPS analysis and support by H<sub>2</sub>-TPR results.

#### 3.2.2. VSM analysis

To further study the impact of formation  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and the influence of the magnetic properties, the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>1-y</sub>Mn<sub>y</sub>O<sub>x</sub> catalysts were measured by vibrating sample magnetometer (VSM). The M-H curves of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>1-y</sub>Mn<sub>y</sub>O<sub>x</sub> are shown in Fig. 2(c) and summary of the magnetic properties are shown in Table 3. It is found that the introduction of Mn can enhance the coercivity (M<sub>r</sub>) and saturation magnetization (M<sub>s</sub>) of Fe<sub>1-y</sub>Mn<sub>y</sub>O<sub>x</sub> remarkably. When the doping content of manganese is increased to 15%, the value of M<sub>r</sub> and M<sub>s</sub> reached the maximum value 46.16 emu/g and 5.91 emu/g, respectively. In comparison with  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> that M<sub>r</sub> and M<sub>s</sub> value is 42.05 emu/g and 0.94 emu/g, respectively, Fe<sub>0.85</sub>Mn<sub>0.15</sub>O<sub>x</sub> shows better magnetism. It has been reported that the increase of magnetism can improve the adsorption of NO at low temperature on the catalyst surface because NO is a paramagnetic molecule and degaussing of catalyst at high temperature [15,24,25]. Furthermore, the increased magnetization of Fe<sub>1-y</sub>Mn<sub>y</sub>O<sub>x</sub> is positively related to the promotion of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> formation





**Fig. 2.** (a) XRD spectra of the catalysts; (b) the partial enlarged detail of Fe<sub>0.85</sub>Mn<sub>0.15</sub>O<sub>x</sub> and γ-Fe<sub>2</sub>O<sub>3</sub> (PDF#39-1346); (c) Samples' room-temperature magnetization curves of the catalysts; (d) N<sub>2</sub> adsorption-desorption isotherms of the catalysts; SEM images of (e) α-Fe<sub>2</sub>O<sub>3</sub> and (f) Fe<sub>0.85</sub>Mn<sub>0.15</sub>O<sub>x</sub>.

**Table 2**

Summary of the XRD data analysis of the Fe<sub>1-y</sub>Mn<sub>y</sub>O<sub>x</sub> catalysts and γ-Fe<sub>2</sub>O<sub>3</sub>.

Samples	crystallite sizes (Å)	lattice constants (Å)	γ / (α+γ) Fe <sub>2</sub> O <sub>3</sub> (%)
Fe <sub>0.95</sub> Mn <sub>0.05</sub> O <sub>x</sub>	116	8.34	61.0
Fe <sub>0.90</sub> Mn <sub>0.10</sub> O <sub>x</sub>	132	8.32	63.3
Fe <sub>0.85</sub> Mn <sub>0.15</sub> O <sub>x</sub>	132	8.30	75.8
Fe <sub>0.80</sub> Mn <sub>0.20</sub> O <sub>x</sub>	127	8.31	73.0
γ-Fe <sub>2</sub> O <sub>3</sub>	103	8.36	100

**Table 3**

Summary of the magnetic properties of the samples.

Samples	M <sub>s</sub> (emu/g)	M <sub>r</sub> (emu/g)	H <sub>c</sub> (Oe)
α-Fe <sub>2</sub> O <sub>3</sub>	5.78	0.87	92.44
Fe <sub>0.95</sub> Mn <sub>0.05</sub> O <sub>x</sub>	33.96	3.14	46.10
Fe <sub>0.90</sub> Mn <sub>0.10</sub> O <sub>x</sub>	36.34	3.90	46.21
Fe <sub>0.85</sub> Mn <sub>0.15</sub> O <sub>x</sub>	46.16	5.91	35.37
Fe <sub>0.80</sub> Mn <sub>0.20</sub> O <sub>x</sub>	43.05	4.29	31.45
γ-Fe <sub>2</sub> O <sub>3</sub>	42.05	0.94	14.89

in XRD results and Fe<sub>0.85</sub>Mn<sub>0.15</sub>O<sub>x</sub> show the best catalytic activity, which may be due to the difference of NO adsorption on the surface caused by the magnetism of the catalyst. These factors will be discussed in the in-situ DRIFT results.

### 3.2.3. BET analysis

The specific surface area is an important factor affecting the adsorption capacity of reaction gas on the catalyst. As depicted in Fig. 2 (d) and Fig. S3, the isotherms of the α-Fe<sub>2</sub>O<sub>3</sub>, γ-Fe<sub>2</sub>O<sub>3</sub>, γ-Mn<sub>2</sub>O<sub>3</sub> and Fe<sub>1-y</sub>Mn<sub>y</sub>O<sub>x</sub> catalysts exhibit typical IV curves at high relative pressure and the pore sizes are corresponding to mesoporous material (2–50 nm)

[26,27]. Table 4 summarizes the surface physical properties of the pure Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>1-y</sub>Mn<sub>y</sub>O<sub>x</sub> catalysts. Combined with XRD quantitative analysis, the γ Fe<sub>2</sub>O<sub>3</sub> ratio in Fe<sub>1-y</sub>Mn<sub>y</sub>O<sub>x</sub> catalysts increasing with the Mn mole ratio from 5% to 15%. As summarized in Table 4, the specific surface areas of γ-Fe<sub>2</sub>O<sub>3</sub> and γ-Mn<sub>2</sub>O<sub>3</sub> are 125 and 55 m<sup>2</sup>/g, respectively, which is much larger than that of α-Fe<sub>2</sub>O<sub>3</sub> (23 m<sup>2</sup>/g). When doped into α-Fe<sub>2</sub>O<sub>3</sub> the Mn mole ratio is 15%, the specific surface area is largest and reaches 85 m<sup>2</sup>/g, which is enlarge ca. 370% to the α-Fe<sub>2</sub>O<sub>3</sub>. This shows that the formation of γ-Fe<sub>2</sub>O<sub>3</sub> significantly affects the specific surface area of the catalyst. The average pore size of Fe<sub>0.85</sub>Mn<sub>0.15</sub>O<sub>x</sub> is 14 nm, corresponding to lessen ca. 36% in comparison with the α-Fe<sub>2</sub>O<sub>3</sub>. Beyond this value, with the Mn mole ratio is increased to 20% the surface area lessened from 85 to 57 m<sup>2</sup>/g, indicating that doping of excessive manganese may segregate MnO<sub>x</sub> nanoparticles lead to the collapse or sintering of the pore structure, will lead to an lessen in the specific surface area of the catalyst. Generally, NO conversion is related to specific surface area of catalyst in NH<sub>3</sub>-SCR, as shown in Fig. 1(a). Interestingly, Fe<sub>0.95</sub>Mn<sub>0.05</sub>O<sub>x</sub> and Fe<sub>0.90</sub>Mn<sub>0.10</sub>O<sub>x</sub> catalysts have similar specific surface areas, 53 m<sup>2</sup>/g and 52 m<sup>2</sup>/g respectively, but the NH<sub>3</sub>-SCR activity at low temperature is quite different. The NO conversion of Fe<sub>0.90</sub>Mn<sub>0.10</sub>O<sub>x</sub> catalyst is 96.6% while Fe<sub>0.95</sub>Mn<sub>0.05</sub>O<sub>x</sub>

**Table 4**

Summary of the structural properties of the samples.

Materials	Specific surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore Size (nm)
α-Fe <sub>2</sub> O <sub>3</sub>	23	0.12	22
Fe <sub>0.95</sub> Mn <sub>0.05</sub> O <sub>x</sub>	53	0.28	18
Fe <sub>0.90</sub> Mn <sub>0.10</sub> O <sub>x</sub>	52	0.21	17
Fe <sub>0.85</sub> Mn <sub>0.15</sub> O <sub>x</sub>	85	0.29	14
Fe <sub>0.80</sub> Mn <sub>0.20</sub> O <sub>x</sub>	57	0.22	16
γ-Fe <sub>2</sub> O <sub>3</sub>	125	0.45	14
γ-Mn <sub>2</sub> O <sub>3</sub>	55	0.19	11

catalyst is only 63.6% at 100 °C, which may be related to the magnetism of the catalyst.

### 3.2.4. SEM and EDS analysis

To elaborate examine the  $\text{Fe}_{1-y}\text{Mn}_y\text{O}_x$  and  $\alpha\text{-Fe}_2\text{O}_3$  structure, SEM observation were used for understand the structure of the  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  catalysts and results are shown in Fig. 2(e) and (f). It can be seen that the surface morphology of  $\alpha\text{-Fe}_2\text{O}_3$  presents smooth spherical particle accumulation, and its particle size is 1–3  $\mu\text{m}$ . After modified the  $\text{Fe}_2\text{O}_3$  crystal structure by introducing Mn, the smooth sphere was dispersed into smaller spheres, showing more surface defects, and its particle size was obviously smaller than that of  $\alpha\text{-Fe}_2\text{O}_3$ . This structural change will increase the specific surface area of the catalyst, which is beneficial to the adsorption of  $\text{NH}_3$  and  $\text{O}_2$ , thus improving the removal efficiency of  $\text{NO}_x$ . This result is consistent with  $\text{N}_2$  adsorption-desorption curve data and support by  $\text{NH}_3/\text{O}_2$ -TPD results. Moreover, EDS mapping were tested to further explore the distribution of Mn species on the  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  catalyst. Fig S4 shows elemental maps of Fe, Mn and O on the  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  catalyst. From the signal intensity of Mn in the Fig S4(d) is much lower than that of Fe, it can be seen that Mn species are highly dispersed in the  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  catalyst. The EDS mapping results also confirm the homogeneous dispersion of Mn species and Fe co-located in the doped samples.

### 3.3. Redox properties

The redox property of the catalyst is crucial to the  $\text{NH}_3$ -SCR reaction activity at low temperature. For this reason,  $\text{H}_2$ -TPR and  $\text{O}_2$ -TPD was used to analyze the redox property of the  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\gamma\text{-Fe}_2\text{O}_3$ ,  $\gamma\text{-Mn}_2\text{O}_3$  and  $\text{Fe}_{1-y}\text{Mn}_y\text{O}_x$  catalysts, with the  $\text{H}_2$ -TPR results shown in Fig. 3(a) and  $\text{H}_2$  consumption peaks area are summarized in Table 5. All asymmetric peaks are deconvoluted by the by Gaussian-Lorenz function. For the  $\alpha\text{-Fe}_2\text{O}_3$ , composing only of the octahedral  $\text{Fe}^{3+}(\text{Fe}_{\text{Oh}}^{3+})$  site, two visible peaks are observed at about 381 and 620 °C, which correspond to consecutive reduction process:  $\text{Fe}_{(\text{Oh})2}\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$  [28,29]. Different from  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\gamma\text{-Fe}_2\text{O}_3$  consisting of  $\text{Fe}_{\text{Td}}^{3+}$  and  $\text{Fe}_{\text{Oh}}^{3+}$  sites and  $\text{Fe}_{\text{Td}}^{3+}$  sites is more active in redox reaction at low temperatures [7,9,30,31]. Therefore,  $\gamma\text{-Fe}_2\text{O}_3$  has two peaks around 352 and 409 °C, which correspond to the reduction of  $\text{Fe}_{(\text{Th})2}\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$  and  $\text{Fe}_{(\text{Oh})2}\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ , respectively. In addition, the peak around 586 °C corresponds to the reduction of  $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$  [7,9,30,31]. The two peaks of  $\gamma\text{-Mn}_2\text{O}_3$  at 317 and 452 °C correspond to the reduction of  $\text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4$  and  $\text{Mn}_3\text{O}_4 \rightarrow \text{MnO}$ , respectively. In comparison with the  $\alpha\text{-Fe}_2\text{O}_3$ , two reduction peaks at 381 and 620 °C shift to 361 and 556 °C in the  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$ , respectively. Combine with the  $\text{Fe}_{1-y}\text{Mn}_y\text{O}_x$  catalysts XRD and XPS results, spinel structure coupled with two new reduction peak of  $\text{Fe}_{1-y}\text{Mn}_y\text{O}_x$  is observed at  $\sim 297$  and 330 °C, which is attribute to the  $\text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4$  and  $\text{Fe}_{(\text{Td})2}\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$  in  $\text{Fe}_{1-y}\text{Mn}_y\text{O}_x$  catalysts. Because the shift of the peak position to a lower temperature represents the improvement of the reduction properties of the catalyst [32]. With increase the  $\text{Mn}^{3+}$  content from 5% to 15%, it can be apparently observed that the peaks area of  $\text{Fe}_{(\text{Oh})2}\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$  ( $\sim 380$  °C) is decrease and shift to lower temperatures and the peak area of  $\text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4$  gradually increases at  $\sim 300$  °C. It suggests that substitution  $\text{Fe}_{(\text{Oh})}^{3+}$  with  $\text{Mn}^{3+}$  to form  $\text{Mn}_{(\text{Oh})}^{3+}$  can facilitate the reduction process of  $\text{Fe}_{(\text{Oh})}$

$2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$  by electron transfer between  $\text{Mn}^{3+}$  and  $\text{Fe}^{3+}$ . However, there has no obvious influence the reduction peaks area change of  $\text{Fe}_{(\text{Th})2}\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$  ( $\sim 330$  °C), more importantly, the decreasing reduction peak areas of  $\text{Fe}_{(\text{Oh})2}\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$  approximate increasing peak areas of  $\text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4$ , which is significant evidence that the  $\text{Fe}^{3+}$  sites substituted with  $\text{Mn}^{3+}$  are  $\text{Fe}_{\text{Oh}}^{3+}$  sites rather than  $\text{Fe}_{\text{Td}}^{3+}$  sites in  $\gamma\text{-Fe}_2\text{O}_3$  of  $\text{Fe}_{1-y}\text{Mn}_y\text{O}_x$  catalysts. This is consistent with the previous XRD analysis.

The  $\text{O}_2$ -TPD curves of  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\gamma\text{-Fe}_2\text{O}_3$ ,  $\gamma\text{-Mn}_2\text{O}_3$  and  $\text{Fe}_{1-y}\text{Mn}_y\text{O}_x$  catalysts are shown in Fig. 3(b). Four  $\text{O}_2$  desorption peaks are observed at  $\sim 200$ ,  $\sim 300$ ,  $\sim 450$  and  $\sim 530$  °C in  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{Fe}_{1-y}\text{Mn}_y\text{O}_x$  catalysts with the temperature increasing from 100 to 650 °C. For  $\gamma\text{-Fe}_2\text{O}_3$ , two peaks are observed at 263 and 412 °C, and three peaks appear at 197, 375 and 543 °C were detected in  $\gamma\text{-Mn}_2\text{O}_3$ . The peaks at  $\sim 100$ –300 °C are assigned to chemically adsorbed oxygen ( $\text{O}_{\text{abs}}$ ,  $\text{O}_{(\text{abs})}^{\cdot}$ ) denoted as  $\text{O}_{\alpha}$  while the peaks at  $\sim 300$ –600 °C are assigned to lattice oxygen ( $\text{O}_{\text{latt}}^2$ ) denoted as  $\text{O}_{\beta}$ , among which the  $\text{O}_{\alpha}$  are related to surface oxygen defect [4]. The  $\text{O}_{\alpha}$  peaks area and position were summarized in the Table 6, compared with  $\gamma\text{-Fe}_2\text{O}_3$ ,  $\alpha\text{-Fe}_2\text{O}_3$  and  $\gamma\text{-Mn}_2\text{O}_3$  show small  $\text{O}_{\alpha}$  peak area, which indicates that  $\gamma\text{-Fe}_2\text{O}_3$  has more oxygen vacancies. Furthermore, the  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  exhibits the largest area of  $\text{O}_{\alpha}$  peak among the  $\text{Fe}_{1-y}\text{Mn}_y\text{O}_x$  catalysts. This corresponds to the fact that  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  has the highest content of  $\gamma\text{-Fe}_2\text{O}_3$  among the  $\text{Fe}_{1-y}\text{Mn}_y\text{O}_x$  catalysts in the previous XRD analysis, showing that introduction of Mn promoted the formation of  $\gamma\text{-Fe}_2\text{O}_3$  is conducive to generate more surface oxygen defect. The oxygen defect has been reported that favorable for promoting the redundant electrons transferred to the different metal ions surrounding the oxygen vacancy thus facilitating oxidation of NO to  $\text{NO}_2$  [4,33,34], which is in accord with XPS and in-situ DRIFT results.

### 3.4. Acidity properties

$\text{NH}_3$ -TPD studies were conducted to characterize the surface acidity of the  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\gamma\text{-Fe}_2\text{O}_3$ ,  $\gamma\text{-Mn}_2\text{O}_3$  and  $\text{Fe}_{1-y}\text{Mn}_y\text{O}_x$  catalysts. As shown in Fig. 4(a), for  $\alpha\text{-Fe}_2\text{O}_3$  and  $\gamma\text{-Mn}_2\text{O}_3$ , the low intensity peaks are observed at about 210 and 196 °C, respectively, demonstrating the poor  $\text{NH}_3$  desorption and less acidic sites of  $\alpha\text{-Fe}_2\text{O}_3$  and  $\gamma\text{-Mn}_2\text{O}_3$ , the profiles of  $\text{Fe}_{1-y}\text{Mn}_y\text{O}_x$  catalysts and  $\gamma\text{-Fe}_2\text{O}_3$  can be divide into two peaks at  $\sim 105$  and  $\sim 200$  °C, previous studies have shown that  $\text{NH}_3$  desorption peaks appeared in the range of 100–150 and 150–350 °C are assigned to the physical adsorption of  $\text{NH}_3$  and weak acidity, respectively [32,35]. As shown in Fig. 4(b), compared with  $\alpha\text{-Fe}_2\text{O}_3$ , it was clear that the  $\text{NH}_3$  desorption amounts of  $\text{Fe}_{1-y}\text{Mn}_y\text{O}_x$  catalysts and  $\gamma\text{-Fe}_2\text{O}_3$  were much higher than the  $\alpha\text{-Fe}_2\text{O}_3$  and  $\gamma\text{-Mn}_2\text{O}_3$ , suggesting that incorporation of Mn formation of  $\gamma\text{-Fe}_2\text{O}_3$  contribute to the increase of acidic sites on the  $\text{Fe}_{1-y}\text{Mn}_y\text{O}_x$  catalysts surface, which can enhance the NO conversion on  $\text{Fe}_{1-y}\text{Mn}_y\text{O}_x$  in the  $\text{NH}_3$ -SCR reaction.

It is generally recognized that coordinate  $\text{NH}_2$  species and Brønsted acid is decisive for the  $\text{NH}_3$ -SCR LT activity [1,36]. In situ DRIFTS of  $\text{NH}_3$  adsorption-desorption is conducted to differentiate Lewis (denoted as L) acid and Brønsted (denoted as B) acid, and the results are shown in Fig. 4 (c) and Fig. 4(d). Several bands were appeared after  $\text{NH}_3$  coordinated with acidic sites on the  $\alpha\text{-Fe}_2\text{O}_3$  and  $\gamma\text{-Fe}_2\text{O}_3$  catalyst surface. As the previous studies were shown that the bands appear at 1141, 1225 and 1600  $\text{cm}^{-1}$  attributed to  $\text{NH}_3$  species adsorbed on the L-acid sites, while the bands at 1351, 1374 and 1553, 1577  $\text{cm}^{-1}$  could be classified as the

**Table 5**

$\text{H}_2$  consumption peak area of each phase in various catalysts.

Samples	$\text{Fe}_{(\text{Oh})2}\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$	$\text{Fe}_{(\text{Td})2}\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$	$\text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4$	Total $\text{H}_2$ consumption
$\alpha\text{-Fe}_2\text{O}_3$	3944	–	–	4944
$\text{Fe}_{0.95}\text{Mn}_{0.05}\text{O}_x$	1301	2054	502	3857
$\text{Fe}_{0.90}\text{Mn}_{0.10}\text{O}_x$	953	2024	1016	3993
$\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$	156	2033	1722	3911
$\text{Fe}_{0.80}\text{Mn}_{0.20}\text{O}_x$	488	2003	1462	3953
$\gamma\text{-Fe}_2\text{O}_3$	2015	4022	–	6037
$\gamma\text{-Mn}_2\text{O}_3$	–	–	4822	4822

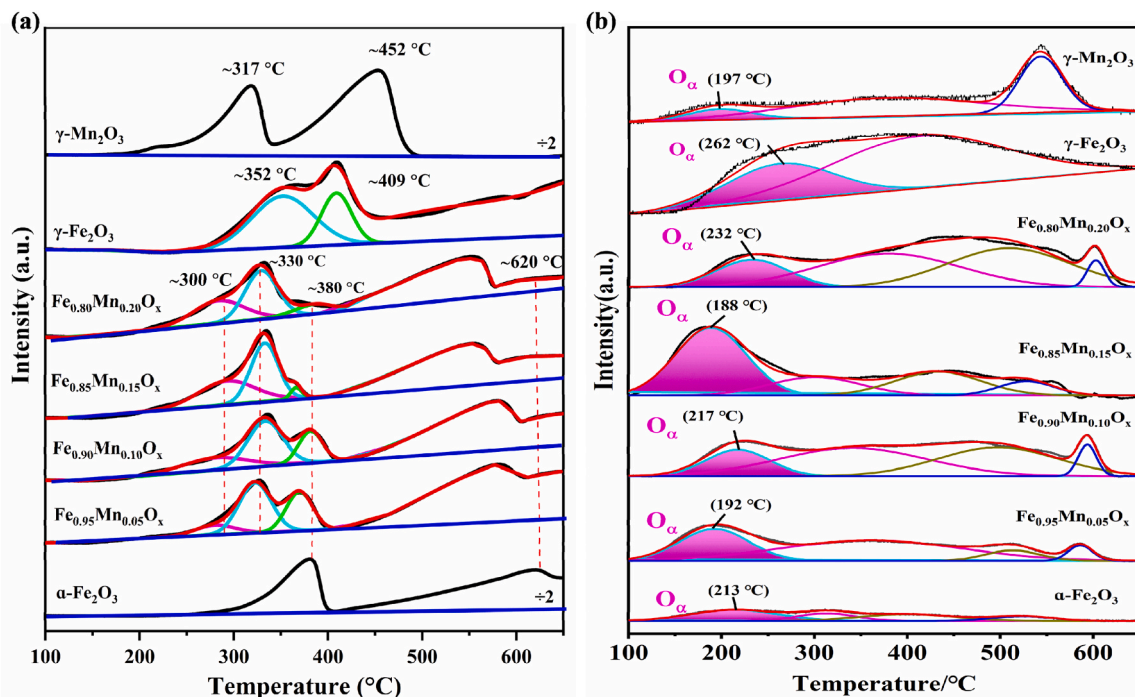


Fig. 3.  $\text{H}_2$ -TPR (a) and  $\text{O}_2$ -TPD (b) profiles of catalysts.

Table 6

The  $\text{O}_\alpha$  peak area and position of catalysts.

Samples	Position (°C)	Area
$\alpha\text{-Fe}_2\text{O}_3$	213	494
$\text{Fe}_{0.95}\text{Mn}_{0.05}\text{O}_x$	192	1122
$\text{Fe}_{0.90}\text{Mn}_{0.10}\text{O}_x$	217	859
$\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$	188	2456
$\text{Fe}_{0.80}\text{Mn}_{0.20}\text{O}_x$	232	1000
$\gamma\text{-Fe}_2\text{O}_3$	262	2115
$\gamma\text{-Mn}_2\text{O}_3$	197	369

$\text{NH}_2$  species and  $\text{NH}_2$  species coordinated to L-acid, respectively [37, 38]. It should be pointed out that the peaks at 1425 and 1462  $\text{cm}^{-1}$  belonging to Brønsted acid site in the  $\gamma\text{-Fe}_2\text{O}_3$ , which are not observed in the spectrum of  $\alpha\text{-Fe}_2\text{O}_3$ . For the  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  catalyst, the bands appear at 1140, 1194, and 1600  $\text{cm}^{-1}$  could be assigned to the L acid site while the bands at 1451 and 1643  $\text{cm}^{-1}$  are  $\text{NH}_4^+$  ions attached to the B acid site. It is obvious that  $\text{NH}_3$  adsorption-desorption bands of  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  are similar but have some differences. Compared with  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  has extra acid site 1194 (L acid) and 1451, 1643  $\text{cm}^{-1}$  (B acid), indicating that introduction of Mn formation of  $\gamma\text{-Fe}_2\text{O}_3$  is conducive to the formation of B-acid sites. Besides, 1360 and 1573  $\text{cm}^{-1}$  are related to the  $\text{NH}_2$  and  $\text{NH}_2$  species, respectively. Active  $\text{NH}_2$  species from oxidative dehydrogenation of  $\text{NH}_3$  are essential intermediates for E-R reaction and establish acid cycle on the catalyst surface [9,17,39]. The bands assigned to  $\text{NH}_2$  (1360  $\text{cm}^{-1}$ ) and  $\text{NH}_2$  (1573  $\text{cm}^{-1}$ ) species can be detected on the surface of  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  and  $\gamma\text{-Fe}_2\text{O}_3$  at 50 °C. This shows that the acid cycle of  $\text{NH}_3$  and E-R reaction on  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  and  $\gamma\text{-Fe}_2\text{O}_3$  can be carried out at a lower temperature than that of  $\alpha\text{-Fe}_2\text{O}_3$ .

### 3.5. Surface chemical state

The surface atomic composition and valence state distribution of the catalyst are crucial to understand the redox cycle in  $\text{NH}_3$ -SCR, hence XPS measurements of  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  and  $\alpha\text{-Fe}_2\text{O}_3$  were conducted and the results are displayed in Fig. 5 and Table 7. All asymmetric peaks are

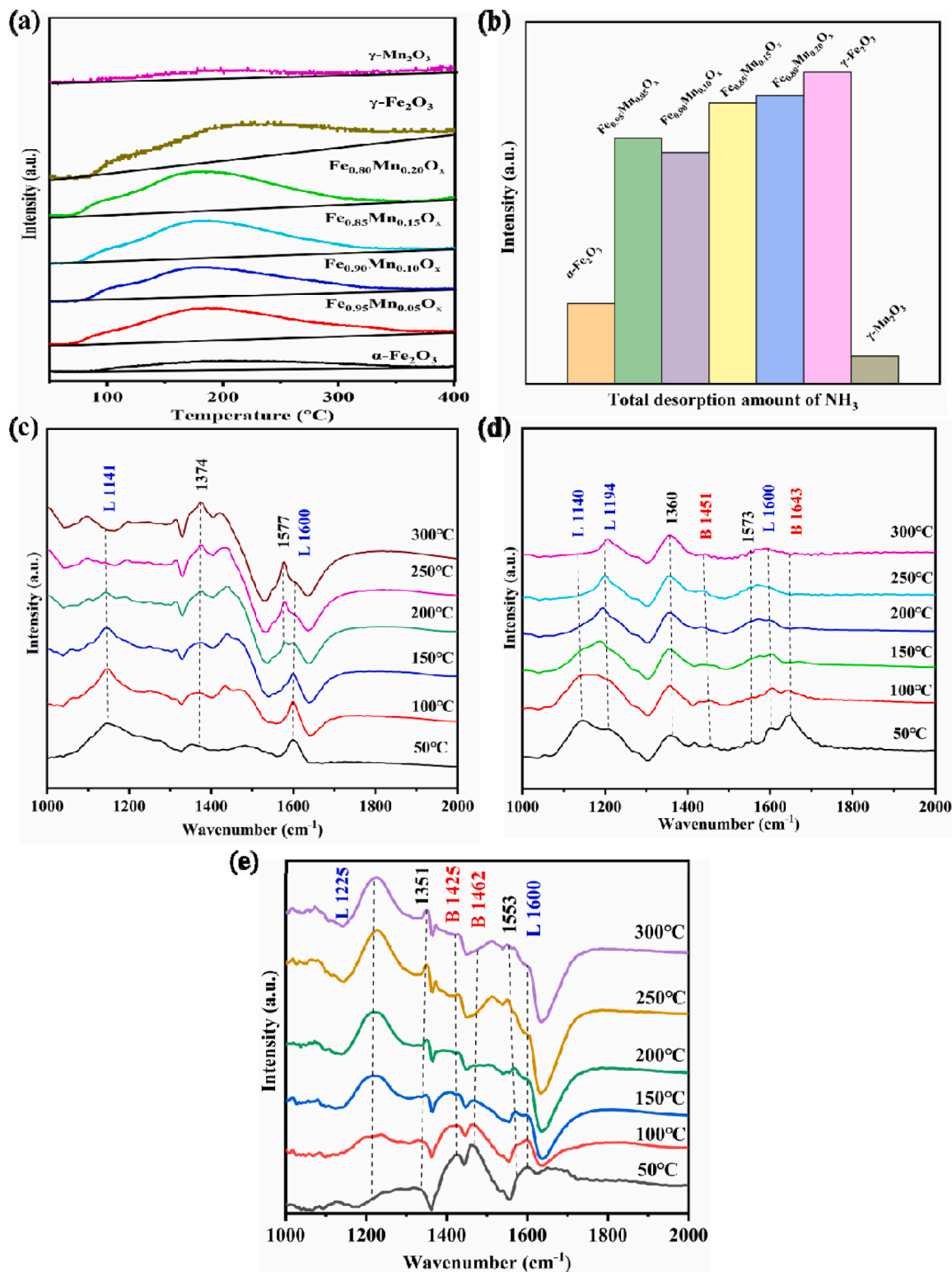
deconvoluted by the Gaussian-Lorentz function. As displayed in Fig. 5(a), for  $\alpha\text{-Fe}_2\text{O}_3$ , the peaks arise at 709.5 and 711.1 eV, which were attached to  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , respectively [4,40,41]. It can be observed that compare to the  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  peak position of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , shifted from 709.5 to 709.7 eV and 711.1–711.5 eV higher binding energy, respectively, revealing that exist electrons transferred between Mn and Fe in  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$ . This electron transfer and interaction is also reflected in the XRD and  $\text{H}_2$ -TPR results. Fig. 5(b) shows the XPS spectra of Mn 2p, the peaks located at 641.2 and 643.4 eV were assigned to the  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$ , respectively [39]. The O 1s spectra of  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  in Fig. 5(c) were fitted into two peaks, chemically adsorbed oxygen ( $\text{O}_{\text{ads}}$ ,  $\text{O}_{\text{ads}}$ ) denoted as  $\text{O}_\alpha$  (531.6 eV) and lattice oxygen ( $\text{O}_{\text{latt}}$ ,  $\text{O}_{\text{latt}}$ ) denoted as  $\text{O}_\beta$  (529.7 eV) [4,42,43]. Moreover, compared with  $\alpha\text{-Fe}_2\text{O}_3$ , the  $\text{O}_\beta$  peak shift from 529.8 to 529.6 eV lower binding energy was detected on  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  sample, which may result from the electron transfer in the strong interaction between Fe-O-Mn after Mn substituting part inactive  $\text{Fe}_{\text{OH}}$  sites of  $\alpha\text{-Fe}_2\text{O}_3$ . As summarized in Table 7, compare  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  and  $\alpha\text{-Fe}_2\text{O}_3$ , the percent of  $\text{O}_\alpha$  on  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  clearly increases from 15.3% to 45.4%, respectively, which immensely enhances the redox capacity of  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  catalyst. More importantly, compare to  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$ , the percent of  $\text{Fe}^{3+}$  and  $\text{Mn}^{3+}$  were decrease while the percent of  $\text{Fe}^{2+}$ ,  $\text{Mn}^{4+}$  and  $\text{O}_\alpha$  were increase on  $\alpha\text{-Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  surface. According to previous researches, the oxygen vacancy by accelerating the transfer of redundant electrons from metal ions ( $\text{Fe}^{3+}$ ,  $\text{Mn}^{3+}$ ) hence facilitating the formation of  $\text{Fe}^{2+}$  and  $\text{Mn}^{4+}$  ions, which is consistent with our experimental observation and proves that the redox cycle between  $\text{Fe}^{3+} + \text{Mn}^{3+} \leftrightarrow \text{Fe}^{2+} + \text{Mn}^{4+}$  of  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  exist in  $\text{NH}_3$ -SCR reaction.

### 3.6. In-situ DRIFT tests

#### 3.6.1. $\text{NO} + \text{O}_2$ adsorption-desorption

In-situ DRIFTS test of  $\text{NO} + \text{O}_2$  adsorption-desorption were carried out due to investigate the  $\text{NO}_x$  active species on the catalyst surface at different temperatures is indispensable for revealing the reaction mechanism. As shown in Fig. 6(a), the surface of  $\alpha\text{-Fe}_2\text{O}_3$  adsorbed species of linear nitrite (1078  $\text{cm}^{-1}$ ), monodentate nitrate (1286  $\text{cm}^{-1}$ ) and bridged nitrate (1600  $\text{cm}^{-1}$ ) are observed at 50 °C. As the





**Fig. 4.** (a) NH<sub>3</sub>-TPD patterns of catalysts; (b) Total desorption amount of NH<sub>3</sub>; In-situ DRIFTS spectra of NH<sub>3</sub> adsorption-desorption: (c)  $\alpha\text{-Fe}_2\text{O}_3$ , (d)  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  and (e)  $\gamma\text{-Fe}_2\text{O}_3$ .

temperature rises, the intensity of monodentate nitrate weakens while new peaks of bidentate nitrate (1547, 1570  $\text{cm}^{-1}$ ) and bridged nitrite (1206  $\text{cm}^{-1}$ ) are observed at 150–300 °C [8,35,44]. The results show that with the increase of temperature, monodentate nitrate species gradually transform into quite stable NO<sub>x</sub> species. Distinguish from  $\alpha\text{-Fe}_2\text{O}_3$ , the bands of monodentate nitrate (1436  $\text{cm}^{-1}$ ) can form on  $\gamma\text{-Fe}_2\text{O}_3$  surface at 50 °C. Besides, with the temperature rises from 150 to

300 °C, all the bands intensity significantly weakens, which indicates that NO<sub>x</sub> species formed on the surface of  $\gamma\text{-Fe}_2\text{O}_3$  are unstable at 150–300 °C. For  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$ , as exhibited in Fig. 6(b), the bands relating to bridged nitrite (1197  $\text{cm}^{-1}$ ), NO<sub>2</sub> (1622  $\text{cm}^{-1}$ ) and monodentate nitrate (1434  $\text{cm}^{-1}$ ) can be observed on the  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  surface at 50 °C, indicating that the NO<sub>2</sub> and bridged nitrite can be generated from oxidation of NO at low temperatures. Among active NO<sub>x</sub> species, NO<sub>2</sub>



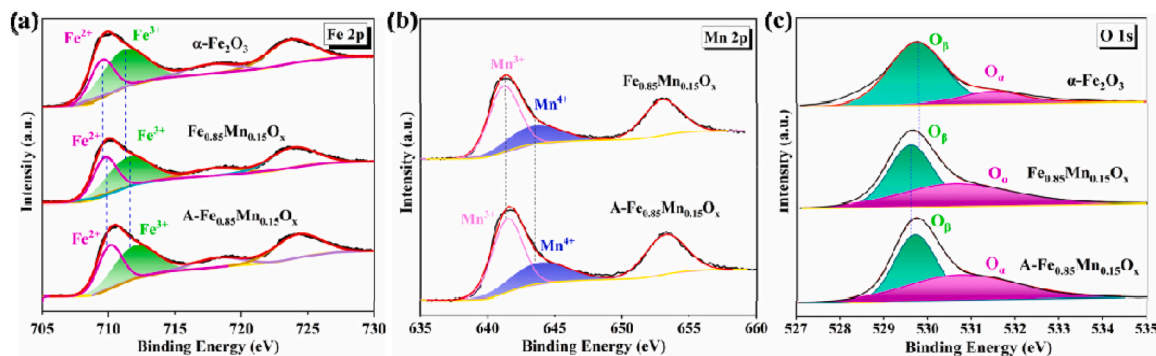


Fig. 5. XPS spectra of  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  (after  $\text{NH}_3$ -SCR reaction denoted as A- $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$ ) and  $\alpha\text{-Fe}_2\text{O}_3$ : (a) Fe 2p, (b) Mn 2p, (c) O 1s.

Table 7

Surface atomic concentration of  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  (after  $\text{NH}_3$ -SCR reaction denoted as A- $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$ ) and  $\alpha\text{-Fe}_2\text{O}_3$ .

Samples Atomic Concentration (mol%)	$\text{Fe}_{\text{total}}$		$\text{Mn}_{\text{total}}$		$\text{O}_{\text{total}}$	
$\alpha\text{-Fe}_2\text{O}_3$	28.5		–		71.5	
$\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$	19.9		10.5		69.6	
A- $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$	19.9		10.7		69.4	
Atomic Ratio (%)	$\text{Fe}^{3+}/$ ( $\text{Fe}_{\text{total}}$ )	$\text{Fe}^{2+}/$ ( $\text{Fe}_{\text{total}}$ )	$\text{Mn}^{3+}/$ ( $\text{Mn}_{\text{total}}$ )	$\text{Mn}^{4+}/$ ( $\text{Mn}_{\text{total}}$ )	$\text{O}_{\alpha}/$ ( $\text{O}_{\text{total}}$ )	$\text{O}_{\beta}/$ ( $\text{O}_{\text{total}}$ )
$\alpha\text{-Fe}_2\text{O}_3$	65.5	34.5	–	–	15.3	84.7
$\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$	58.8	41.2	65.9	34.1	45.4	54.6
A- $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$	57.4	42.6	63.8	36.2	48.8	51.2

from NO oxidation can significantly boost LT  $\text{NH}_3$ -SCR activity by inducing Fast SCR reaction [45,46]. Moreover, the bridged nitrite ( $1197\text{ cm}^{-1}$ ) and  $\text{NO}_2$  ( $1622\text{ cm}^{-1}$ ) decrease with increasing temperature and then vanish at  $200^\circ\text{C}$ , while the peak intensity of bridged nitrate ( $1248\text{ cm}^{-1}$ ) and bidentate nitrate ( $1572\text{ cm}^{-1}$ ) arise at  $150^\circ\text{C}$ , indicating that bridged nitrite can be transform to bridged nitrate and bidentate nitrate at  $150^\circ\text{C}$ . Previous study indicated bidentate nitrates are inactive at low temperatures while became active at high temperatures [47]. It is worth noting that monodentate nitrate, bridged nitrate and bidentate nitrate weaken with the temperatures over  $200^\circ\text{C}$ , indicating that  $\text{NO}_x$  species more easier form equilibrium of formation-decomposition on  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  surface than  $\alpha\text{-Fe}_2\text{O}_3$  at  $50\text{--}300^\circ\text{C}$ . This phenomenon is similar to the  $\gamma\text{-Fe}_2\text{O}_3$  and consistent with the previously reported that magnetism affects the adsorption of NO at low temperature and the analysis of our VSM experimental results. Commonly, the SCR activity decrease with formation of steady  $\text{NO}_x$  species by cause of covering active sites on the catalyst surface [48]. This discrepancy formation of  $\text{NO}_x$  species and its thermal stability on the  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  and  $\alpha\text{-Fe}_2\text{O}_3$  surface may be one of the crucial factors leading to the excellent LT  $\text{NH}_3$ -SCR activity of  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  at  $50\text{--}300^\circ\text{C}$ .

### 3.6.2. $\text{NH}_3+\text{NO}+\text{O}_2$ co-adsorption

The reaction mechanism of  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\gamma\text{-Fe}_2\text{O}_3$  and  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  was further investigated by  $\text{NH}_3+\text{NO}+\text{O}_2$  co-adsorption. As shown in Fig. 7 (a), several bands assigned to linear nitrite ( $1080\text{ cm}^{-1}$ ), monodentate nitrate ( $1282$ ,  $1482\text{ cm}^{-1}$ ), bridged nitrate ( $1226$ ,  $1609\text{ cm}^{-1}$ ),  $\text{NH}_2$  species ( $1572\text{ cm}^{-1}$ ) and bridged nitrite ( $1202\text{ cm}^{-1}$ ) can be observed on the  $\alpha\text{-Fe}_2\text{O}_3$  of  $\text{NH}_3+\text{NO}+\text{O}_2$  co-adsorption. However, the bands relevant to  $\text{NH}_3$  adsorption didn't appear and the monodentate nitrate and bridged nitrite species quite stable on the  $\alpha\text{-Fe}_2\text{O}_3$  surface at below  $150^\circ\text{C}$ . According to previous research, competitive adsorption between  $\text{NH}_3$  and  $\text{NO}+\text{O}_2$  exists and  $\text{NO}+\text{O}_2$  was on  $\alpha\text{-Fe}_2\text{O}_3$  preferential adsorption [8,47]. That means that the adsorbed  $\text{NO}_x$  species and  $\text{NH}_3$  is difficult to occur reaction on  $\alpha\text{-Fe}_2\text{O}_3$  at low temperatures. As shown in Fig. 7(a), compared with  $\alpha\text{-Fe}_2\text{O}_3$ , the bands attribute to  $\text{NH}_4^+$  ions coordinated with B-acid sites ( $1438\text{ cm}^{-1}$ ),  $\text{NH}_2$  ( $1364\text{ cm}^{-1}$ ) and  $\text{NH}_2$

species ( $1572\text{ cm}^{-1}$ ) can observe on  $\gamma\text{-Fe}_2\text{O}_3$  surface at  $50^\circ\text{C}$ . In addition, the bands intensity relevant to  $\text{NH}_3$  adsorption gradually weakened and disappeared at  $200^\circ\text{C}$ , which indicates that the acidic sites formed on  $\gamma\text{-Fe}_2\text{O}_3$  surface can react with  $\text{NO}_x$  species. After Mn modified  $\text{Fe}_2\text{O}_3$ , as shown in Fig. 7(b), the bands corresponding to bridged nitrite ( $1206\text{ cm}^{-1}$ ),  $\text{NO}_2$  ( $1614\text{ cm}^{-1}$ ),  $\text{NH}_4^+$  ions coordinated with B-acid sites ( $1465\text{ cm}^{-1}$ ),  $\text{NH}_2$  ( $1364\text{ cm}^{-1}$ ),  $\text{NH}_2$  specie ( $1516\text{ cm}^{-1}$ ) and  $\text{NH}_4\text{NO}_2$  ( $1078\text{ cm}^{-1}$ ) can be observed on the  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  surface at  $50^\circ\text{C}$ . Furthermore, the peaks intensity of bridged nitrite,  $\text{NH}_4^+$  ions and  $\text{NO}_2$  rapidly decline from  $50$  to  $100^\circ\text{C}$ , indicating that the Fast SCR reaction is able to occur on  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  at low temperature. Besides, the overlapping peaks of  $\text{NH}_2$  species ( $1516\text{ cm}^{-1}$ ) and  $\text{NH}_4^+$  ions coordinated with B-acid sites ( $1465\text{ cm}^{-1}$ ) at  $200\text{--}300^\circ\text{C}$  were identified. Remarkably, there is no bands relevant to  $\text{NO}+\text{O}_2$  while the bands intensity corresponding to  $\text{NH}_3$  coordinated with the L-acid and B-acid sites became stronger with temperature from  $200$  to  $300^\circ\text{C}$ , which is mainly because high temperature promotes the oxidative dehydrogenation of  $\text{NH}_3$  on  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$ .

### 3.6.3. Reactivity of adsorbed species on $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$

In-situ DRIFTS instantaneous reaction were proposed to explore the reaction intermediates of  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  in low temperature  $\text{NH}_3$ -SCR reaction. The  $\text{NH}_3$  was pre-adsorbed on  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  surface for 1 h at  $100^\circ\text{C}$  and  $\text{NO}+\text{O}_2$  was introduced to react with the adsorbed  $\text{NH}_3$  species after the  $\text{N}_2$  purge for 0.5 h. As shown in Fig. 8(a), several bands assigned to coordinated  $\text{NH}_3$  with L-acid ( $1086$ ,  $1120$ , and  $1602\text{ cm}^{-1}$ ),  $\text{NH}_4^+$  ions adsorbed on B-acid sites ( $1640\text{ cm}^{-1}$ ) and N-H vibration of the adsorbed  $\text{NH}_3$  ( $3374\text{ cm}^{-1}$ ) can be observed on the  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  surface after adsorption of  $\text{NH}_3$  [8,35,44,47]. Moreover, with introducing  $\text{NO}+\text{O}_2$  that the bands attributed to  $\text{NH}_3$  species disappear immediately and the wide bands attributed to O-H ( $3400\text{--}3600\text{ cm}^{-1}$ ) was emerged gradually, showing that the introduced NO can directly react with the adsorbed ammonia species to occur Eley-Rideal (E-R) reaction pathway at low temperatures. Furthermore, the bands attributing to  $\text{NO}_2$  ( $1626\text{ cm}^{-1}$ ) can be detected gradually (3 min later), according to previous research which can react with  $\text{NH}_4^+$  to occur Langmuir-Hinshelwood (L-H) reaction pathway and then form  $\text{NH}_4\text{NO}_2$

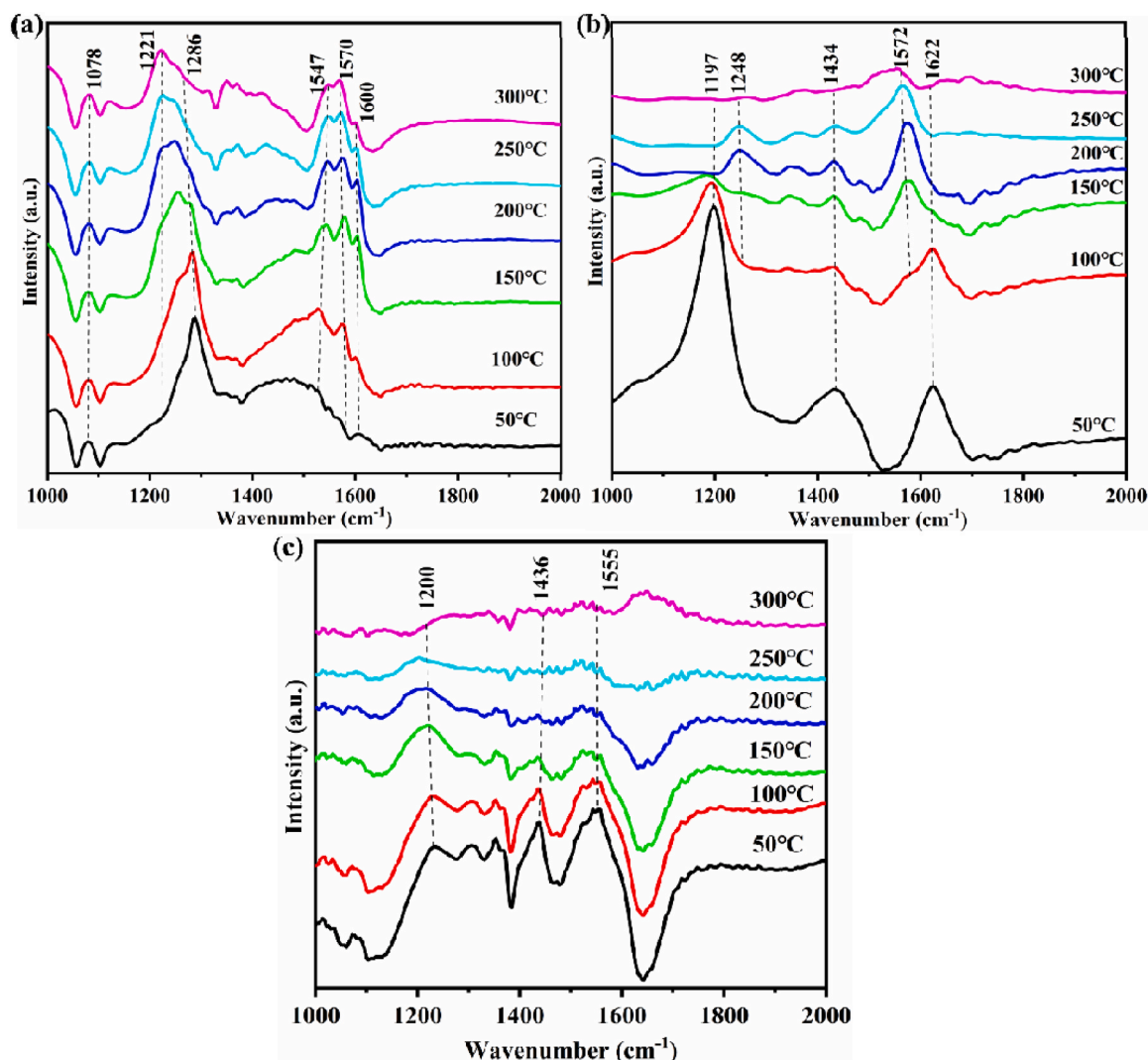


Fig. 6. In-situ DRIFTS spectra of NO+O<sub>2</sub> adsorption-desorption for catalysts: (a) α-Fe<sub>2</sub>O<sub>3</sub>, (b) Fe<sub>0.85</sub>Mn<sub>0.15</sub>O<sub>x</sub> and (c) γ-Fe<sub>2</sub>O<sub>3</sub>.

that rapid generation of N<sub>2</sub> and H<sub>2</sub>O (Fast SCR).

The transformation between adsorbed NH<sub>3</sub> species and reaction with pre-adsorbed NO<sub>x</sub> species is further studied by in-situ DRIFTS studies that NO+O<sub>2</sub> pre-adsorbed and followed by NH<sub>3</sub> adsorption on Fe<sub>0.85</sub>Mn<sub>0.15</sub>O<sub>x</sub> at 100 °C. As shown in Fig. 8(b), the bridged nitrite (1194 cm<sup>-1</sup>) and NO<sub>2</sub> (1621 cm<sup>-1</sup>) are clearly observed on Fe<sub>0.85</sub>Mn<sub>0.15</sub>O<sub>x</sub> surface after NO+O<sub>2</sub> pre-adsorbed. When the NH<sub>3</sub> is introduced, the bands of bridged nitrite, NO<sub>2</sub> and O-H (3400–3600 cm<sup>-1</sup>) vanish gradually and several bands assigned to coordinated NH<sub>3</sub> with L-acid sites (1154, 1254, 1284 and 1602 cm<sup>-1</sup>), N-H (3374 cm<sup>-1</sup>) and NH<sub>4</sub><sup>+</sup> ions adsorbed on B-acid sites (1445, 1631 cm<sup>-1</sup>) can be observed [8,32, 35,38]. Furthermore, NH<sub>2</sub> (1565 cm<sup>-1</sup>) can be detected after 1 min, indicating that NH<sub>3</sub> can be rapidly oxidized to active NH<sub>2</sub> at low temperature. [31,32,47]. Notably, compare with Fig. 8(a), the bands intensity of B-acid sites (1445 cm<sup>-1</sup>) and NH<sub>2</sub> (1565 cm<sup>-1</sup>) are obvious became stronger than NH<sub>3</sub> species adsorption alone, indicating that chemically adsorbed oxygen and adsorbed NO<sub>x</sub> species is promotes the formation of B-acid sites and NH<sub>2</sub>. Moreover, the intensity of NH<sub>2</sub> (1565 cm<sup>-1</sup>) gradually weaken while the B-acid sites (1445 cm<sup>-1</sup>) became stronger in 5 min, indicating that the conversion between NH<sub>2</sub> (1565 cm<sup>-1</sup>) and B-acid sites (1445 cm<sup>-1</sup>) in the acid cycle.

### 3.7. Reaction mechanism

After substituted part inactive Fe<sub>OH</sub><sup>3+</sup> sites of Fe<sub>2</sub>O<sub>3</sub> with active Mn<sub>OH</sub><sup>3+</sup>, the Fe<sub>2</sub>O<sub>3</sub> crystal structure generate more active Fe<sup>3+</sup> CASSs. The establishment of redox cycle Fe<sup>3+</sup>+Mn<sup>3+</sup> ↔ Fe<sup>2+</sup>+Mn<sup>4+</sup> between Fe-O-Mn induced the increase of chemically adsorbed oxygen on the Fe<sub>0.85</sub>Mn<sub>0.15</sub>O<sub>x</sub> surface, not only boosted the formation of NO<sub>2</sub> but also facilitated the Brønsted acid circle. Based on the results analysis, possible a reaction mechanism that over Fe<sub>0.85</sub>Mn<sub>0.15</sub>O<sub>x</sub> are proposed and the model are depicted in Fig. 9. In this mechanism, chemisorbed oxygen (O<sub>abs</sub>) reacts with Fe(III) to form the Fe(III)-O<sup>-</sup> reactive intermediates. Subsequently, NH<sub>3</sub> adsorbed on Fe(III)-O<sup>-</sup> groups proceed oxidative dehydrogenation reaction to produce active Fe(III)-OH-NH<sub>2</sub> intermediates. The activated -NH<sub>2</sub> groups derived from Fe(III)-OH-NH<sub>2</sub> intermediates could occur Eley-Ridea (E-R) reaction pathway with gaseous NO to generate NH<sub>2</sub>-NO intermediate that generation of N<sub>2</sub>, H<sub>2</sub>O and generate Fe(III)-OH sites. The NH<sub>3</sub> adsorbed on Fe(III)-OH sites to occur redox reaction and then form Fe(II)-ONH<sub>4</sub><sup>+</sup> sites. This catalytic reaction process included the electronic transfer the redox cycle between Fe<sup>3+</sup>+Mn<sup>3+</sup> ↔ Fe<sup>2+</sup>+Mn<sup>4+</sup>, the NO<sub>2</sub> is induced to form at low temperature and then reaction with the Fe(II)-ONH<sub>4</sub><sup>+</sup> to have Fast SCR. The active Fe(III)-O<sup>-</sup> groups were regenerated through the redox cycle between Fe<sup>3+</sup>+Mn<sup>3+</sup> ↔ Fe<sup>2+</sup>+Mn<sup>4+</sup> to complete redox cycle and acid cycle. This cycle also occurs at the Mn<sub>OH</sub><sup>3+</sup> active sites.

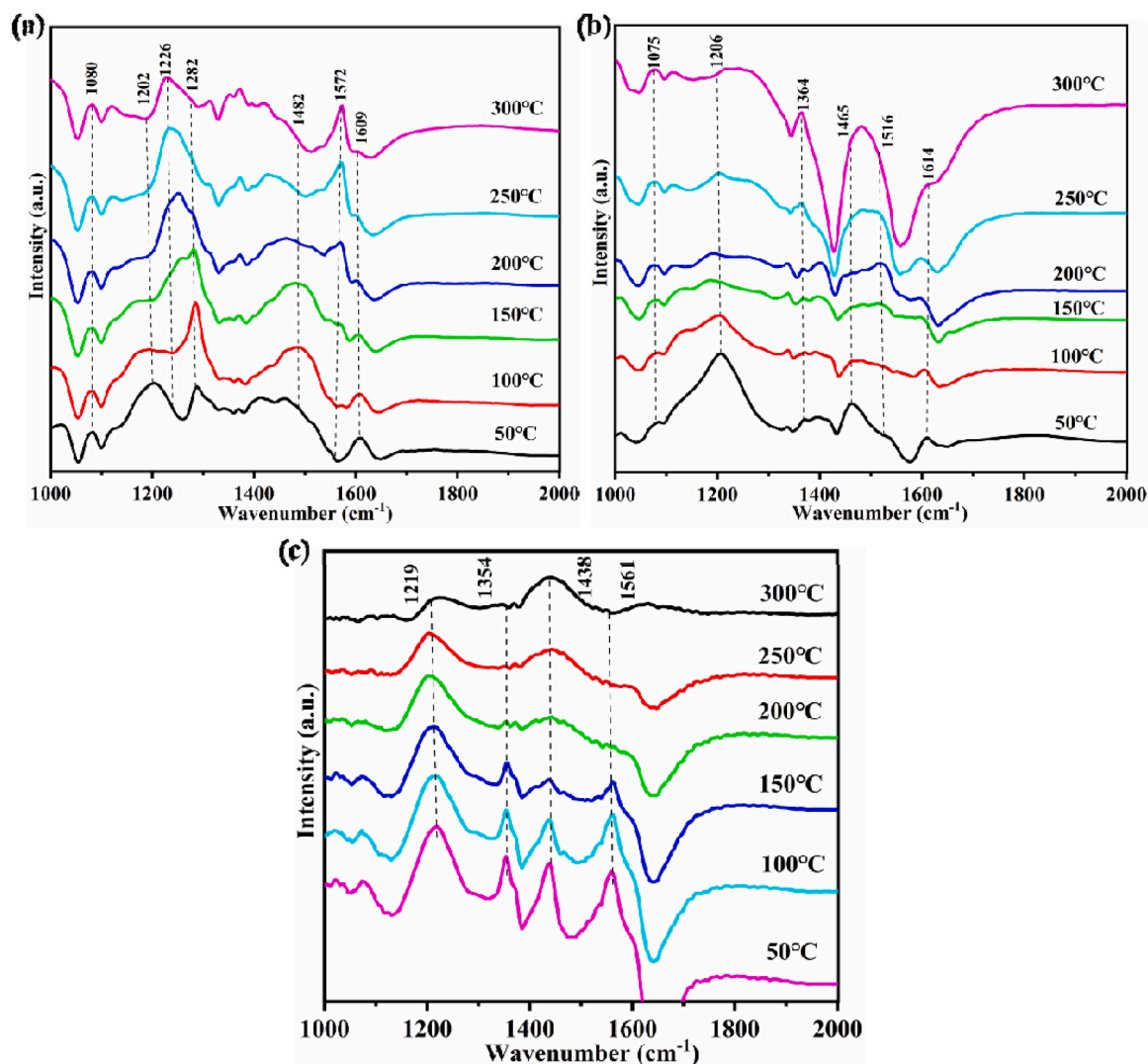


Fig. 7. In-situ DRIFTS spectra of (a)  $\alpha$ - $\text{Fe}_2\text{O}_3$ , (b)  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  and (c)  $\gamma$ - $\text{Fe}_2\text{O}_3$   $\text{NH}_3$ + $\text{NO}$ + $\text{O}_2$  co-adsorption.

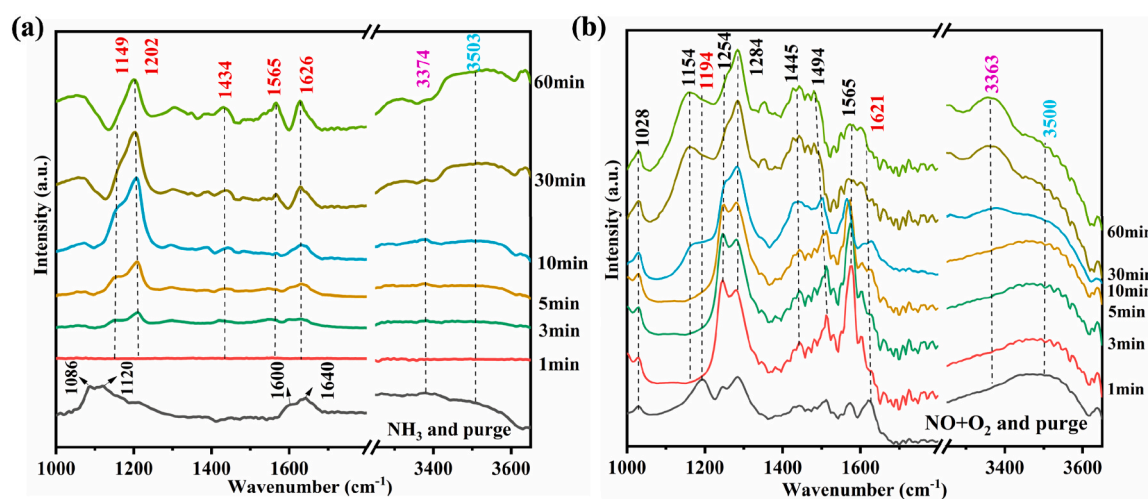


Fig. 8. In-situ DRIFTS spectra of  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  at 100 °C. (a)  $\text{NH}_3$  pre-adsorption and then introduced  $\text{NO}+\text{O}_2$ , (b)  $\text{NO}+\text{O}_2$  pre-adsorption and then introduced  $\text{NH}_3$ .

#### 4. Conclusions

In this work, a highly LT  $\text{NH}_3$ -SCR activity and an extensive reaction

window catalyst by Mn modified the  $\alpha$ - $\text{Fe}_2\text{O}_3$  crystal structure has been composed by using sol-gel strategy. The transition of  $\alpha$ - $\text{Fe}_2\text{O}_3$  to the  $\gamma$ - $\text{Fe}_2\text{O}_3$  structure and magnetic properties are promoted after

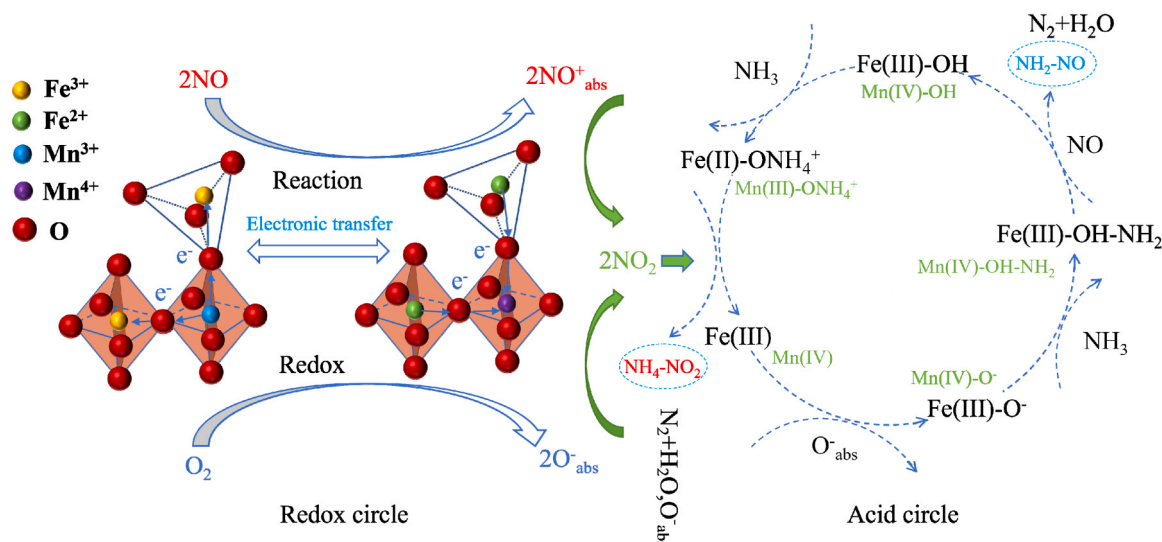


Fig. 9. Reaction mechanism model for  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$ .

substituted part inactive  $\text{Fe}_{\text{Oh}}^{3+}$  sites of  $\text{Fe}_2\text{O}_3$  with active  $\text{Mn}_{\text{Oh}}^{3+}$  sites. Besides, introducing of highly dispersed  $\text{Mn}^{3+}$  into the  $\gamma\text{-Fe}_2\text{O}_3$  crystal-line structure to generate Fe-O-Mn coordinate sites, which can increase of chemically adsorbed oxygen and then enhanced the oxidation of NO and  $\text{NH}_3$  on the  $\text{Fe}_{0.85}\text{Mn}_{0.15}\text{O}_x$  surface to facilitate the redox circle and acid cycle at low temperatures. It is of great significance to deepen the understanding relationship between crystal structure and CASs of  $\alpha\text{-Fe}_2\text{O}_3$  and  $\gamma\text{-Fe}_2\text{O}_3$ , designing of high-performance catalysts of SCR catalysts at low temperatures.

#### CRediT authorship contribution statement

**Donghai Mo:** Conceptualization, Investigation, Methodology, Formal analysis, Writing – original draft, Data curation. **Qiuju Qin:** Resources, Formal analysis, Validation, Visualization. **Chengheng Huang:** Validation, Formal analysis, Software, Visualization. **Lin Tao:** Software, Visualization, Resources. **Chen Li:** Validation, Formal analysis. **Jiaqi Qiu:** Validation, Visualization. **Jingkai Wang:** Formal analysis, Software. **Xiaorong Han:** Validation, Visualization. **Shifei Gu:** Validation, Visualization. **Zhengjun Chen:** Funding acquisition, Supervision. **Bin Li:** Funding acquisition, Supervision. **Lihui Dong:** Funding acquisition, Project administration, Supervision.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data Availability

Data will be made available on request.

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#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2024.123869](https://doi.org/10.1016/j.apcatb.2024.123869).

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